Chemical Physics Letters 544 (2012) 13–16

Contents lists available at SciVerse ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

The nuclear electric quadrupole moment of hafnium from the molecular method

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ARTICLE INFO

Article history:
Received 29 May 2012
In final form 1 July 2012
Available online 7 July 2012

ABSTRACT

The molecular method is used to obtain nuclear electric quadrupole moment (NQM) values for hafnium through electric field gradients (EFGs) at this nucleus in HfO and HfS. Dirac–Coulomb calculations with the Coupled Cluster approach, DC-CCSD (T) and DC-CCSD-T, were carried out to achieve the most accurate estimates of these EFGs. Higher order corrections are also added. Hence, the most reliable values for ^{177}Hf and ^{179}Hf determined here are 3319(33) and 3750(37) mbarn, respectively, in nice accordance with the best currently accepted NQMs for this element.

1. Introduction

The molecular method is used to determine nuclear quadrupole moments (NQMs) by means of theoretical results for electric field gradients (EFGs) at the nucleus investigated and experimental nuclear quadrupole coupling constants (NQCCs) from rotational spectra. Hence, the NQM, $Q(X)$, of a given nucleus X in a linear molecule, in barns, is

$$Q(X) = \frac{\nu_Q(X)}{234.9647\ q(X)}, \quad (1)$$

in which $\nu_Q(X)$ and $q(X)$ are, respectively, the NQCC (in MHz) and the EFG (in a.u.) of such nucleus. This method usually results in an average value for the NQM that is obtained from a group of molecules containing the atom under study. Fortunately, experimental NQCCs for hafnium in HfO and HfS are available [1–3]. Moreover, the crucial importance of a precise treatment of relativistic effects and electron correlation during the calculation of EFGs to be used in the molecular method has been extensively discussed in the literature [4–7] and the Density Functional Theory (DFT) with common exchange-correlation functionals is usually not adequate unless in an indirect method [8].

The molecular method is used in this Letter to attain the NQMs for two isotopes of hafnium, ^{177}Hf and ^{179}Hf. The Hamiltonians considered in EFG calculations are Dirac–Coulomb (DC) and Dirac–Coulomb–Gaunt (DG). Analytic EFG values are obtained from Hartree–Fock (HF) and DFT methods with B3LYP and BPW91 exchange-correlation functionals. However, the most accurate EFG determinations were done with the Coupled Cluster method including single and double substitutions iteratively and perturbative treatments of triple excitations [9,10], DC-CCSD (T) and DC-CCSD-T. The Gaussian set selected for hafnium was the relativistic adapted Gaussian basis set, RAGBS [11], which is free of variational prolapse and was obtained from the polynomial generator coordinate Dirac–Fock (p-GCDF) method [12]. Higher order corrections from Gaunt and larger active space contributions were also summed into these EFGs. These larger active space calculations are done with perturbation theory at the MP2 level.

2. Computational details

The general procedure performed to obtain EFGs for hafnium in this Letter is similar to that already employed before for antimony [6] and lutetium [7]. Hence, the light speed value used in these calculations is 137.0359998 a.u. The Gaussian nuclear model was also employed here [13] and small component integrals were replaced by an interatomic correction to reduce the computational cost [14]. The basis sets chosen are cc-pVTZ and cc-pVQZ sets for oxygen [15] and sulfur [16] and the RAGBS for hafnium [11], which were always used in the uncontracted form. The RAGBS for hafnium can also be found at http://basis-sets.iqsc.usp.br/relativistic-basis-sets/relativistic-adapted-gaussian-basis-sets-ragbss. Moreover, experimental values of equilibrium bond lengths for HfO and HfS are 1.7231 and 2.1561 Å, respectively [2,3], and EFGs were determined in these geometries.

Finally, calculations were carried out with the DIRAC11 package [17]. However, since convergence difficulties were observed with DIRAC11 for these molecules, DIRAC10 and DIRAC08 packages [18,19] were also employed mainly to provide coefficients that are used as initial guess for further calculations that were done with DIRAC11.

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http://dx.doi.org/10.1016/j.cplett.2012.07.002

3. Results and discussion

3.1. Basis set augmentation

The RAGBS for hafnium, which comprises 30*s*22*p*17*d*11*f* functions, was firstly used in an investigation of augmentation by diffuse and tight s, p, d and f functions. Hence, calculations were done at the DC-HF and DC-B3LYP levels and analytic EFGs obtained during this process at the hafnium nucleus in HfO were compared. Both cc-pVTZ and cc-pVQZ sets for oxygen are considered. The exponents of these new functions added to hafnium were found by extrapolations from p-GCDF parameters adjusted for this atom [11]. The sequential augmentation process by an increasing number of functions was carried out individually for all combinations of tight or diffuse and *s* or *p* or *d* or *f* symmetries. Functions capable of changing this EFG by more than 0.007 a.u. in any of the calculation levels were selected at this stage. The exponents of chosen functions are presented between parenthesis along the text and Table 1 shows EFG values encountered in this convergence study in combination with the cc-pVTZ basis set for oxygen. Hence, two diffuse *p* (0.09207363161 and 0.03197204309) and one diffuse *f* (0.1493424377) functions were inserted into the original basis set resulting in an intermediate set for hafnium named a-RAGBS (augmented RAGBS) with size 30*s*24*p*17*d*12*f*. Curiously, the diffuse functions of hafnium that resulted in EFG differences above the threshold in calculations with cc-pVTZ or cc-pVQZ sets for oxygen were exactly the same.

Further, polarization *g* functions with the same exponents of available *d* functions were added sequentially to a-RAGBS from the most diffuse available to tighter members. Again, the same threshold was used to choose functions to be maintained. The group of *g* functions selected included all functions from the most diffuse that yielded relevant EFG changes in any of the calculation levels until a tight one after which the convergence was ensured by adding two more tighter functions that should result in EFG changes below the threshold or else the procedure continued. This resulted in 5*g* functions for hafnium (3.998520969, 1.981450240, 0.9419124877, 0.4246206456 and 0.1794627837) in combination with the cc-pVTZ set of oxygen leading to a-RAGBS-5 g for hafnium. However, 8*g* functions are chosen for hafnium (55.03115478, 28.71532934, 15.04819009, 7.829600488, 3.998520969, 1.981450240, 0.9419124877 and 0.4246206456) in calculations using the cc-pVQZ set for oxygen and a-RAGBS-8 g is obtained. Although the convergence criterion was already met in this last case by using only 4 *g* functions, the other 4 tightest *g* members were also maintained since they still show a relevant collective effect on EFG values.

The procedure was repeated once again starting from the previous sets (a-RAGBS-5 g and a-RAGBS-8 g) by adding now *h* functions with exponents taken from existing *f* functions. The same two *h* functions were selected (2.025976790 and 0.9345376106) in calculations with cc-pVTZ or cc-pVQZ sets for oxygen, resulting in two final basis sets for hafnium. The largest one, 30*s*24*p*17*d*12*f*8*g*2*h*, is used together with the cc-pVQZ set to obtain all the analytic values of EFGs. The smallest one, 30*s*24*p*17*d*12*f*5*g*2*h*, is suitable for finite-difference calculations along with the cc-pVTZ set due to computational cost reasons. However, it is interesting to notice that the difference in EFG values for these two choices in DC-HF and DC-B3LYP is only 0.022 and 0.028 a.u., respectively, and more negative EFG values are derived from the smallest basis sets.

3.2. Nuclear quadrupole coupling constants

NQCCs of HfO are available for vibrational levels up to $v = 5$ [2]. Hence, NQCCs corresponding to the equilibrium condition, that are required in Eq. (1) since EFGs are calculated at equilibrium geometries, were determined after a linear regression and the values obtained are −5968.6 and −6744.8 MHz respectively for ^{177}HfO and ^{179}HfO.

On the other hand, only one NQCC value obtained at $v = 0$ was measured for HfS [3]. However, by using an equation shown in Ref. [5], that requires some available experimental data [20] along with calculated quantities such as first and second derivatives of EGFs with respect to changes in bond lengths and the NQM given by HfO results, a correction can be estimated for NQCCs in order to account for this difference. Hence, by using DC-BPW91 and DC-B3LYP calculations of analytic EFG values for HfS with the largest basis sets in the experimental equilibrium geometry and in four distorted geometries (±0.005 and ±0.010 Å), a correction to this NQCC is determined. The values obtained at the DC-BPW91 (−6.0 MHz) and DC-B3LYP (−5.8 MHz) levels for ^{177}HfS are averaged, resulting in a very small correction that represents only 0.1% of the total NQCC. For comparison, the difference between the NQCC value associated with equilibrium and the experimental one at $v = 0$ for ^{177}HfO is a little bit larger, −15.7 MHz, what is not surprising.

Table 1
Electric field gradients at the hafnium nucleus (in atomic units) obtained during the basis set convergence study for hafnium in HfO in combination with the cc-pVTZ basis set for oxygen.

Basis set	DC-HF		DC-B3LYP		Basis set	DC-HF		DC-B3LYP	
	q (Hf)	Δq (Hf)	q (Hf)	Δq (Hf)		q (Hf)	Δq (Hf)	q (Hf)	Δq (Hf)
30*s*22*p*17*d*11*f*	−7.714		−7.889		a-RAGBS[b]	−8.275		−8.050	
+1 tight *s*	−7.714	−0.0002	−7.889	−0.0003	+1 *g*	−8.275	0.0003	−8.050	0.0000
+1 tight *p*	−7.713	0.0012	−7.888	0.0011	+2 *g*[a]	−8.287	−0.0124	−8.056	−0.0059
+1 tight *d*	−7.713	0.0012	−7.891	−0.0019	+3 *g*[a]	−8.320	−0.0322	−8.073	−0.0171
+1 tight *f*	−7.711	0.0029	−7.887	0.0023	+4 *g*[a]	−8.321	−0.0014	−8.073	−0.0001
+1 diffuse *s*	−7.716	−0.0014	−7.889	0.0001	+5 *g*[a]	−8.310	0.0112	−8.062	0.0102
+1 diffuse *p*[a]	−8.219	−0.5044	−8.022	−0.1328	+6 *g*[a]	−8.301	0.0083	-8.052	0.0100
+2 diffuse *p*[a]	−8.259	−0.0407	−8.040	-0.0182	+7 *g*	-8.295	0.0060	-8.046	0.0065
+3 diffuse *p*	−8.260	−0.0006	−8.040	−0.0002	+8 *g*	−8.291	0.0043	−8.041	0.0054
+1 diffuse *d*	−7.713	0.0008	−7.885	0.0042	a-RAGBS-5g[c]	−8.302		−8.053	
+1 diffuse *f*[a]	−7.946	−0.2322	−8.030	−0.1409	+1 *h*	−8.297	0.0047	−8.052	0.0010
+2 diffuse *f*	−7.948	−0.0017	−8.025	0.0046	+2 *h*[a]	−8.284	0.0127	−8.043	0.0089
					+3 *h*[a]	−8.274	0.0099	−8.030	0.0133
					+4 *h*	−8.269	0.0056	−8.023	0.0067
					+5 *h*	−8.265	0.0042	−8.019	0.0046

[a] Selected functions.
[b] Basis set for hafnium with size 30*s*24*p*17*d*12*f*.
[c] Basis set for hafnium with size 30*s*24*p*17*d*12*f*5*g*.

3.3. Finite-difference calculations

In order to obtain estimates of electron correlation contributions to EFGs at calculation levels for which analytic expressions are not implemented in DIRAC11 (DC-CCSD and its variations), the finite-difference method was used. This method requires two extra calculations with an applied field with strength of 1.0×10^{-7} a.u., which is the same value already employed successfully for antimony and lutetium [6,7].

Moreover, after some tests, the 2 tightest p functions were also removed from the smallest basis set of hafnium to avoid instabilities in numerical results obtained. Hence, the basis sets used are cc-pVTZ for oxygen and sulfur and the 30s22p17d12f5g2h set for hafnium. Finally, the active space selected for finite-difference calculations included all spinors with energy between −5 and 21 a.u., which encloses a total of 32 electrons. A similar choice of the active space was also employed for lutetium [7]. These 32 electrons account for 83% of the total analytic EFG for HfO at the DC-HF level.

Moreover, EFG contributions from finite-differences were also calculated at the DC-MP2 level with the same active space already discussed and also with a larger choice that includes all electrons and spinors up to 100 a.u. However, since DC-MP2 and DC-CCSD finite-difference contributions to EFGs found for the smallest active space differ significantly for both HfO and HfS, the correction to this larger active space (Δq_{CCSD}) is scaled to be proportional to DC-CCSD results according to an equation similar to the one found in Ref. [5],

$$\Delta q_{CCSD} = \left(\frac{q_{CCSD,val}}{q_{MP2,val}}\right)\left(q_{MP2,all} - q_{MP2,val}\right), \tag{2}$$

in which $q_{CCSD,val}$ and $q_{MP2,val}$ refer to the contributions to EFGs obtained with the smallest active space in DC-CCSD and DC-MP2 calculations while $q_{MP2,all}$ is the DC-MP2 result with the largest active space. This same correction is added to DC-CCSD, DC-CCSD (T) and DC-CCSD-T estimates of EFGs.

3.4. Nuclear quadrupole moment

EFGs calculated in this Letter are in Table 2. Analytic values were obtained at DC-HF, DC-BPW91, DC-B3LYP and DG-HF levels. One can see that the electron correlation increases substantially the EFGs. The effect of contributions due to the Gaunt operator (DG-HF) is also associated with an increase of EFGs that reaches 1% for HfO and 0.8% for HfS. Hence, these are significantly larger contributions than the largest ones already observed for antimony (0.2%) and lutetium (0.5%) for instance [6,7]. Hence, the Gaunt correction can not be neglected if one intends to obtain accurate EFGs to be used in the molecular method for hafnium. The effect of the full Breit term on EFG values was also investigated before for AuF [21]. The authors noticed by using small basis sets that the retardation part leads to a decrease in the contribution to EFGs at gold in this molecule from 0.065 (Gaunt) to 0.050 (Breit) a.u. Hence, this study on AuF provides a strong evidence that the Gaunt part alone is enough to account for almost all the contribution ascribed to the full Breit term to EFG values for even heavier nuclei than that of hafnium.

Table 2
Electric field gradients and contributions from electron correlation treatments to these gradients at the hafnium nucleus (in atomic units).

Method	HfO	HfS
DC-HF[a]	−8.253	−7.565
DG-HF[a]	−8.173	−7.505
DC-B3LYP[a]	−8.002	−6.824
DC-BPW91[a]	−7.847	−6.614
DC-MP2[b]	0.990	1.285
DC-MP2[b,c]	0.891	1.207
DC-CCSD[b]	0.574	0.765
DC-CCSD (T)[b]	0.559	0.857
DC-CCSD-T[b]	0.600	0.908

[a] Analytic EFG values obtained from the largest basis sets used here (cc-pVQZ for O and S and 30s24p17d12f8g2h for Hf).
[b] Contribution to EFGs from finite-difference estimates using smaller basis sets (cc-pVTZ for O and S and 30s22p17d12f5g2h for Hf).
[c] Considering all electrons and spinors up to 100 a.u. as active space.

Table 3
Nuclear quadrupole moments for ^{177}Hf (in mbarn).

Method	HfO	HfS	Average	MAD
DC-HF	3078	2905	2992	86
DG-HF	3108	2928	3018	90
DC-B3LYP	3174	3221	3198	23
DC-BPW91	3237	3323	3280	43
DC-MP2[a]	3536	3533	3535	2
DC-MP2[a,b]	3488	3490	3489	1
DC-CCSD[a,b]	3318	3239	3278	40
DC-CCSD (T)[a,b]	3311	3283	3297	14
DC-CCSD-T[a,b]	3329	3308	3319	10

[a] With a Gaunt correction estimated at the HF level.
[b] Considering a correction for larger active space contributions obtained at the DC-MP2 level.

The NQMs obtained for ^{177}Hf with the molecular method are arranged in Table 3. First, it is interesting to notice that the absence of electron correlation leads to much larger mean absolute deviations (MADs) between NQM values for the two molecules studied (86 mbarn at the DC-HF level) than results that include this contribution. Moreover, NQM values obtained at the DC-BPW91 and DC-B3LYP levels also show large MADs when compared to more reliable DC-CCSD (T) and DC-CCSD-T methods. However, one can see that the DC-BPW91 average is in agreement with the most precise results. On the other hand, NQMs from DC-MP2 are much larger than those from DC-CCSD (T) and DC-CCSD-T though the MAD for this treatment is only 2 mbarn for the smallest active space.

Finally, one can also notice that the inclusion of triple excitations reduces substantially the MADs and increases the NQMs by 19–41 mbarn. Although results obtained with the two distinct triple substitution treatments are close to each other, the NQMs indicated here are those from DC-CCSD-T once this choice already proved to furnish much better NQMs for antimony [6] and also considering its smaller MAD in comparison with DC-CCSD (T). Hence, the best NQM values obtained here are 3319(33) mbarn for ^{177}Hf and 3750(37) mbarn for ^{179}Hf, in which the last value is given by the relation between experimental NQCCs for the two isotopes in HfO and HfS [2,3]. The error in determined NQMs is estimated as 1%, at most, which is the same value previously suggested for lutetium [7]. The values currently accepted as the best NQMs [22] for these nuclei are 3365(29) and 3793(33) mbarn from muonic measurements [23]. As one can see, though the NQMs obtained here are smaller, the accordance with such values for both isotopes of hafnium is excellent considering the error estimated.

4. Conclusions

The most reliable NQMs obtained here for ^{177}Hf and ^{179}Hf from the molecular method, 3319(33) and 3750(37) mbarn respectively, are those given by EFGs calculated at the DC-CCSD-T level with corrections for a larger active space and for Gaunt contributions. These results constitute the first determination of this quantity for hafnium by means of the molecular method and they are in nice agreement with the values already indicated in 2008 as the best NQMs available for such nuclei [22], which are derived from muo-

nic M X-rays [23]. Hence, this Letter reinforces once again the confidence in the molecular method for the determination of very accurate NQM values.

Acknowledgments

R.L.A.H. acknowledges FAPESP (Brazilian agency) for financial support and CNPq for a research grant.

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